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Hutter, J

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Excited state nuclear forces from the Tamm–Dancoff approximation to time-dependent density functional theory within the plane wave basis set framework

Jürg Hutter[a)]
Physical Chemistry Institute, University of Zurich, Winterthurerstrasse 190, CH-8057 Zurich, Switzerland

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An efficient formulation of time-dependent linear response density functional theory for the use within the plane wave basis set framework is presented. The method avoids the transformation of the Kohn–Sham matrix into the canonical basis and references virtual orbitals only through a projection operator. Using a Lagrangian formulation nuclear derivatives of excited state energies within the Tamm–Dancoff approximation are derived. The algorithms were implemented into a pseudo potential/plane wave code and applied to the calculation of adiabatic excitation energies, optimized geometries and vibrational frequencies of three low lying states of formaldehyde. An overall good agreement with other time-dependent density functional calculations, multireference configuration interaction calculations and experimental data was found. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1540109]

I. INTRODUCTION

In the last several years time-dependent density functional theory (TDDFT)[1] has replaced Hartree–Fock based single-excitation theories as the method of choice for the calculation of vertical excitation energies of medium to large sized molecules.[2,3] Many efficient implementations[4–9] using localized orbital basis sets have been reported. The methods have been tested[10–15] on a wide range of systems and detailed knowledge of the performance of TDDFT for different type of excitations was acquired.

Only recently, Van Caillie and Amos[16,17] have reported the first implementation of property calculations for excited states derived from TDDFT. Their work was followed and extended by Furche and Ahlrichs[18] and Amos.[19] These works state an important starting point for the direct calculation of many experimental quantities. The possibility to efficiently explore excited state surfaces is of key importance for fluorescence spectra and the understanding of photochemical pathways and allows the calculation of vibrational spectra in the harmonic approximation.

Together with the Car–Parrinello[20] method plane waves were recognized as an alternative basis set not only in solid state calculations but also for problems in chemistry.[21] Being an orthogonal, atomic position independent basis plane waves allow for an efficient calculation of nuclear gradients, are not plagued by basis set superposition errors and allow for an unbiased description of the electronic density. This is an especially interesting feature for excited states where often diffuse functions have to be added to localized basis sets. However, all of these advantages come at the cost of a largely increased number of basis functions. Even with the use of pseudopotentials that eliminate the highly localized core functions one to two orders of magnitude larger basis sets are encountered. The shear size of the plane wave basis set makes it necessary to develop specially adapted algorithms. Only then, additional approximations[22] can be avoided and a reasonable computational efficiency achieved. Another advantage of plane wave basis sets is that they naturally include periodic boundary conditions and therefore lead to algorithms for condensed systems. The application of TDDFT to periodic systems is by no means trivial.[23] Nevertheless, having efficient general algorithms available will be very useful for testing new theoretical developments.

In the present paper methods for the calculation of excited states from time-dependent linear response density functional theory are developed. Previous work[24–27] on density functional perturbation theory in the pseudopotential/plane wave basis set framework is adapted for this use. Derivatives of the excited state energy are derived from a Lagrangian formulation[28] and applied to nuclear gradients within the Tamm–Dancoff approximation.[29,30]

II. THEORY

Time-dependent density functional theory has been reviewed by Gross *et al.*[31] and Casida.[2,3] The reader is referred to these articles for the foundations and further details of the theory. In the following the basic equations are given as starting point for the derivation of the algebraic formulas needed for the implementation of the methods within the present framework, i.e., finite set of orthonormal basis functions independent of atomic positions.

A. Time-dependent Kohn–Sham (TDKS) method

Like in the Kohn–Sham (KS) formulation of ground state density functional theory, the density $n(\mathbf{r},t)$ of N interacting electrons in a time-dependent external potential $V_{\text{ext}}(\mathbf{r},t)$ is written in terms of single-particle wave functions $\{\Phi_i(\mathbf{r},t)\}$. For the case of spin-dependent KS theory we have

a)Electronic mail: hutter@pci.unizh.ch

$$n_\sigma(\mathbf{r},t)=\sum_{i=1}^{N_\sigma}\langle\Phi_{i\sigma}|\mathbf{r}\rangle\langle\mathbf{r}|\Phi_{i\sigma}\rangle, \tag{1}$$

where $\sigma=\{\alpha,\beta\}$ labels spin and $N=N_\alpha+N_\beta$. The KS orbitals $\{\Phi(\mathbf{r},t)\}$ have to fulfill an orthonormality constraint

$$\langle\Phi_{i\sigma}|\Phi_{j\sigma}\rangle=\delta_{ij}. \tag{2}$$

The KS orbitals satisfy the time-dependent KS equations

$$\left[-\frac{1}{2}\nabla^2+V_{\mathrm{eff}}^\sigma(\mathbf{r},t)\right]\Phi_{i\sigma}(\mathbf{r},t)=i\frac{\partial}{\partial t}\Phi_{i\sigma}(\mathbf{r},t), \tag{3}$$

where V_{eff}^σ is the local, single-particle potential usually written as

$$V_{\mathrm{eff}}^\sigma(\mathbf{r},t)=V_{\mathrm{ext}}(\mathbf{r},t)+\int d\mathbf{r}'\frac{n(\mathbf{r}',t)}{|\mathbf{r}-\mathbf{r}'|}+V_{\mathrm{xc}}^\sigma[n_\alpha,n_\beta](\mathbf{r},t). \tag{4}$$

The exchange–correlation potential V_{xc} is defined as the functional derivative of the exchange–correlation action A_{xc}, which will be used in the adiabatic approximation[32] and further approximated by the exchange–correlation functional E_{xc} from time-independent KS theory,

$$V_{\mathrm{xc}}^\sigma[n_\alpha,n_\beta](\mathbf{r})=\frac{\delta E_{\mathrm{xc}}[n_\alpha,n_\beta]}{\delta n_\sigma}. \tag{5}$$

B. Linear response and excitation energies in TDKS

Consider a system described in the ground state by the KS orbitals $\{\Phi_i^{\{0\}}\}$ and the KS potential $V_{\mathrm{eff}}(\mathbf{r})$. The corresponding KS equations are

$$F^\sigma|\Phi_{i\sigma}^{\{0\}}\rangle=\sum_{j=1}^{N_\sigma}\epsilon_{ij\sigma}|\Phi_{j\sigma}^{\{0\}}\rangle, \tag{6}$$

where F is the KS Hamiltonian,

$$F^\sigma(\mathbf{r})=-\tfrac{1}{2}\nabla^2+V_{\mathrm{eff}}^\sigma(\mathbf{r}), \tag{7}$$

and ϵ the matrix of Lagrange multipliers,

$$\epsilon_{ij\sigma}=\langle\Phi_{i\sigma}^{\{0\}}|F^\sigma|\Phi_{j\sigma}^{\{0\}}\rangle. \tag{8}$$

The ground state density is defined by

$$n_\sigma^{\{0\}}(\mathbf{r})=\sum_{i=1}^{N_\sigma}\langle\Phi_{i\sigma}^{\{0\}}|\mathbf{r}\rangle\langle\mathbf{r}|\Phi_{i\sigma}^{\{0\}}\rangle. \tag{9}$$

The effect of a harmonic perturbation of frequency ω

$$\delta V(\mathbf{r},t)=\delta V^+(\mathbf{r})e^{i\omega t}+\delta V^-(\mathbf{r})e^{-i\omega t}, \tag{10}$$

on this system is described to first order by

$$\delta V_{\mathrm{eff}}(\mathbf{r},t)=\delta V(\mathbf{r},t)+\delta V_{\mathrm{SCF}}(\mathbf{r},t), \tag{11}$$

where δV_{SCF} is the linear response of the self-consistent field to the change in the charge density δn_σ (in the frequency domain)

$$n_\sigma^{\{1\}}(\mathbf{r},\pm\omega)=\sum_{i=1}^{N_\sigma}\langle\Phi_{i\sigma}^{\{\mp\}}|\mathbf{r}\rangle\langle\mathbf{r}|\Phi_{i\sigma}^{\{0\}}\rangle+\langle\Phi_{i\sigma}^{\{0\}}|\mathbf{r}\rangle\langle\mathbf{r}|\Phi_{i\sigma}^{\{\pm\}}\rangle. \tag{12}$$

The functions $\{\Phi_i^{\{\pm\}}\}$ are the linear response orbitals and can be chosen orthogonal to the subspace of the ground state orbitals

$$\langle\Phi_i^{\{\pm\}}|\Phi_j^{\{0\}}\rangle=0. \tag{13}$$

This choice corresponds to the parallel transport gauge in time-independent density functional perturbation theory. The self-consistent-field response is calculated from the definition of the KS potential,

$$\delta V_{\mathrm{SCF}}^\sigma(\mathbf{r},\pm\omega)=\sum_{\tau=\{\alpha,\beta\}}\int d\mathbf{r}'\left\{\frac{n_\tau^{\{1\}}(\mathbf{r}',\pm\omega)}{|\mathbf{r}-\mathbf{r}'|}+\frac{\delta^2E_{\mathrm{xc}}}{\delta n_\sigma(\mathbf{r})\,\delta n_\tau(\mathbf{r}')}\bigg|_{n^{\{0\}}}\right\}n_\tau^{\{1\}}(\mathbf{r}',\pm\omega). \tag{14}$$

Using results from time-dependent perturbation theory one arrives at the coupled perturbed KS equations

$$\sum_{i,j=1}^{N_\sigma}(\epsilon_{ij\sigma}-(F^\sigma\pm\omega)\,\delta_{ij})|\Phi_{j\sigma}^{\{\pm\}}\rangle=Q^\sigma(\delta V^{\{+\}}+\delta V_{\mathrm{SCF}}^\sigma(\pm\omega))|\Phi_{i\sigma}^{\{0\}}\rangle, \tag{15}$$

where Q^σ is the projector on the subspace of unperturbed unoccupied states

$$Q^\sigma=\mathbf{1}-\sum_{k=1}^{N_\sigma}|\Phi_{k\sigma}^{\{0\}}\rangle\langle\Phi_{k\sigma}^{\{0\}}|. \tag{16}$$

The evaluation of Eq. (15) requires only the occupied unperturbed functions $|\Phi_i^{\{0\}}\rangle$ and their linear response functions $|\Phi_i^{\{\pm\}}\rangle$. The unoccupied space is only referenced through the projectors Q^σ. In addition, the KS orbitals do not have to be in canonical form. This form of the coupled perturbed KS equations has long been recognized as essential in the applications of plane wave based algorithms in density functional perturbation theory.[24]

Excitation energies are determined as poles of the response functions[2] leading to a singular Eq. (15). Therefore, the excitation energies are the solutions to the equations

$$\sum_{i,j=1}^{N_\sigma}(F^\sigma\delta_{ij}-\epsilon_{ij\sigma})|\Phi_{j\sigma}^{\{\pm\}}\rangle+Q^\sigma\delta V_{\mathrm{SCF}}^\sigma(\pm\omega)|\Phi_{i\sigma}^{\{0\}}\rangle=\mp\omega|\Phi_{i\sigma}^{\{\pm\}}\rangle. \tag{17}$$

Note that the Eqs. (15) and (17) for $\Phi_{i\sigma}^{\{\pm\}}$ are each coupled through the definition of δV_{SCF}.

C. Basis set expansion

Expanding the ground state KS orbitals and the linear response orbitals in an orthogonal finite basis set $\{\varphi_p(\mathbf{r})\}$

$$\langle\varphi_p|\varphi_q\rangle=\delta_{pq}, \tag{18}$$

defines the expansion coefficients $\{c_{pi\sigma}^{\{0\}}\}$ and $\{c_{pi\sigma}^{\{\pm\}}\}$,

$$\Phi_{i\sigma}^{\{0\}}(\mathbf{r})=\sum_{p=1}^{M}c_{pi\sigma}^{\{0\}}\varphi_p(\mathbf{r}), \tag{19}$$

$$\Phi_{i\sigma}^{\{\pm\}}(\mathbf{r})=\sum_{p=1}^{M} c_{pi\sigma}^{\{\pm\}}\varphi_p(\mathbf{r}). \tag{20}$$

For the remainder of this paper sums over orbital indices i, j, k,... run over the range 1,...,N_σ and sums over the indices p, q, r,... depicting basis function indices run over all functions 1,...,M.

Using the basis set expansion the operators in Eq. (17) are cast into matrix form

$$\mathbf{F}_{pq\sigma}=\langle\varphi_p|F^\sigma|\varphi_q\rangle, \tag{21}$$

$$\boldsymbol{\epsilon}_{ij\sigma}=\sum_{pq}(c_{pi\sigma}^{\{0\}})^\star\mathbf{F}_{pq\sigma}c_{qj\sigma}^{\{0\}}, \tag{22}$$

$$\mathbf{P}_{pq\sigma}=\sum_{i} c_{pi\sigma}^{\{0\}}(c_{qi\sigma}^{\{0\}})^\star, \tag{23}$$

$$\mathbf{Q}_{pq\sigma}=\delta_{pq}-\mathbf{P}_{pq\sigma}, \tag{24}$$

$$\mathbf{W}_{pq\sigma}=\langle\varphi_p|\delta V_{\mathrm{SCF}}^\sigma|\varphi_q\rangle. \tag{25}$$

It is convenient to introduce the new coefficients x and y,

$$x_{pi\sigma}=\tfrac{1}{2}(c_{pi\sigma}^{\{+\}}+c_{pi\sigma}^{\{-\}}), \tag{26}$$

$$y_{pi\sigma}=\tfrac{1}{2}(c_{pi\sigma}^{\{+\}}-c_{pi\sigma}^{\{-\}}). \tag{27}$$

In the absence of magnetic fields the orbitals can be chosen to be real, therefore $n_\sigma^{\{1\}}(+\omega)=n_\sigma^{\{1\}}(-\omega)$ and $\delta V_{\mathrm{SCF}}^\sigma(+\omega)=\delta V_{\mathrm{SCF}}^\sigma(-\omega)$. Taking suitable linear combinations of Eq. (17) one arrives at a system of equations for the vectors x and y,

$$\sum_{qj}(\mathbf{F}_{pq\sigma}\delta_{ij}-\boldsymbol{\epsilon}_{ij\sigma}\delta_{pq})x_{qj\sigma}+\sum_{qr}\mathbf{Q}_{pr\sigma}\mathbf{W}_{rq\sigma}[n^{\{1\}}]c_{qi\sigma}^{\{0\}} =-\omega y_{pi\sigma}, \tag{28}$$

$$\sum_{qj}(\mathbf{F}_{pq\sigma}\delta_{ij}-\boldsymbol{\epsilon}_{ij\sigma}\delta_{pq})y_{qj\sigma}=-\omega x_{pi\sigma}. \tag{29}$$

Equations (28) and (29) can be cast into the form of a non-Hermitian eigenvalue equation with eigenvalues ω^2 and left and right eigenvectors y and x, respectively,

$$\mathcal{A}(\mathcal{A}+\mathcal{B})\mathbf{x}=\omega^2\mathbf{x}, \tag{30}$$

$$(\mathcal{A}+\mathcal{B})\mathcal{A}\mathbf{y}=\omega^2\mathbf{y}. \tag{31}$$

The (super-) operators $\mathcal{A}$ and $\mathcal{B}$ in Eqs. (30) and (31) are defined as

$$\mathcal{A}_{pi\sigma,qj\tau}=(\mathbf{F}_{pq\sigma}\delta_{ij}-\boldsymbol{\epsilon}_{ij\sigma}\delta_{pq})\,\delta_{\sigma\tau}, \tag{32}$$

$$\mathcal{B}_{pi\sigma,qj\tau}=\sum_{rsuv}\mathbf{Q}_{pr\sigma}c_{ui\sigma}^{\{0\}}\mathcal{K}_{ru\sigma,sv\tau}(c_{vj\tau}^{\{0\}})^\star\mathbf{Q}_{sq\tau}, \tag{33}$$

where $\mathcal{K}$ is the response kernel in the basis set representation

$$\mathcal{K}_{pu\sigma,qv\tau}=\int d\mathbf{r}\,d\mathbf{r}'\;\varphi_p^\star(\mathbf{r})\varphi_u(\mathbf{r})\left[\frac{1}{|\mathbf{r}-\mathbf{r}'|}+\frac{\delta^2E_{\mathrm{xc}}}{\delta n_\sigma(\mathbf{r})\,\delta n_\tau(\mathbf{r}')}\bigg|_{n^{\{0\}}}\right]\varphi_v^\star(\mathbf{r}')\varphi_q(\mathbf{r}'). \tag{34}$$

Note that both operators $\mathcal{A}$ and $\mathcal{B}$ are also projectors on the virtual states and therefore the orthogonality constraint for the solution vectors is fulfilled by construction.

D. Tamm–Dancoff approximation

The Tamm–Dancoff approximation (TDA)[29] leads to the CIS method[33] within time-dependent Hartree–Fock theory. It was first used by Hirata and Head–Gordon[30] within TDDFT and they showed that excitation energies are of the same quality as in full linear response calculations. The TDA results in a Hermitian eigenvalue equation that can be solved using standard iterative techniques. The simpler form of the TDA equations leads to algorithms that have the advantage of better convergence, lower memory requiremnets and only two instead of three superoperator-vector products per iteration. A disadvantage of the TDA is that sum rules are no longer fulfilled[34] leading to poor results for oscillator strength and other related quantities.

The TDA is recovered most easily by setting $c_{ui\sigma}^{\{+\}}=0$ and therefore $x=-y$ in Eq. (28),

$$\sum_{qj}(\mathbf{F}_{pq\sigma}\delta_{ij}-\boldsymbol{\epsilon}_{ij\sigma}\delta_{pq})x_{qj\sigma}+\sum_{qr}\mathbf{Q}_{pr\sigma}\mathbf{W}_{rq\sigma}[n^{\{1\}}]c_{qi\sigma}^{\{0\}} =\omega x_{pi\sigma}, \tag{35}$$

or in superoperator form

$$(\mathcal{A}+\mathcal{B})\mathbf{x}=\omega\mathbf{x}. \tag{36}$$

Equation (36) is a Hermitian eigenvalue equation that is related to the extended energy functional

$$\mathcal{L}_{\mathrm{TDA}}[c^{\{0\}},x,\omega]=\mathbf{x}^\dagger(\mathcal{A}+\mathcal{B})\mathbf{x}-\omega(\mathbf{x}^\dagger\mathbf{x}-1). \tag{37}$$

$\mathcal{L}_{\mathrm{TDA}}$ is variational in x and ω and Eq. (36) is obtained from the variation with respect to $x^\dagger$.

E. Nuclear forces

The calculation of nuclear forces has a long tradition in quantum chemistry.[35] Special techniques have been developed for the cases of nonvariational energy expressions. The Lagrangian method[28] allows for the most compact derivation and will be applied in the following section. The derivative of the total energy of an excited state with respect to an external parameter

$$\frac{dE_{\mathrm{total}}[c^{\{0\}},x]}{d\eta}=\frac{dE_{\mathrm{KS}}[c^{\{0\}}]}{d\eta}+\frac{dE_{\mathrm{TDA}}[c^{\{0\}},x]}{d\eta}, \tag{38}$$

where E_{KS} is the Kohn–Sham energy and E_{TDA} the TDA excitation energy, has to be calculated taking into account all constraints of the wave-function parameters. The Lagrangian function that is variational in all wave-function parameters is

$$\mathcal{L}_{\mathrm{total}}[c^{\{0\}},x,\Lambda,Z,\omega]=\mathcal{L}_{\mathrm{KS}}[c^{\{0\}},\Lambda]+\mathcal{L}_{\mathrm{TDA}}[c^{\{0\}},x,\omega]+\sum_{pi\sigma}\mathbf{Z}_{pi\sigma}\left\{\sum_q\mathbf{F}_{pq\sigma}c_{qi\sigma}^{\{0\}}-\sum_j c_{qj\sigma}^{\{0\}}\Lambda_{ji\sigma}\right\}, \tag{39}$$

where $\mathcal{L}_{\mathrm{KS}}$ is the Lagrange function of the time-independent Kohn–Sham equations,

$$\mathcal{L}_{\mathrm{KS}}[c^{\{0\}},\Lambda]=E_{\mathrm{KS}}[c^{\{0\}}]-\sum_{ij\sigma}\Lambda_{ij\sigma}\left\{\sum_{p}(c^{\{0\}}_{pi\sigma})^{\star}c^{\{0\}}_{pj\sigma}-\delta_{ij}\right\}, \tag{40}$$

$\mathcal{L}_{\mathrm{TDA}}$ was defined in Eq. (37), and Z is the matrix of Lagrange multipliers associated with the stationarity of the Kohn–Sham orbitals. The orthogonality constraint of x with respect to the ground state orbitals is not associated with Lagrange multipliers, but is handled by the projector functions in $\mathcal{L}_{\mathrm{TDA}}$.

It is now assumed that the ground state orbitals are optimized KS orbitals and that x is a solution to Eq. (36). Then the derivative of $\mathcal{L}_{\mathrm{total}}$ with respect to η is

$$\mathcal{L}^{(\eta)}_{\mathrm{total}}=\frac{\partial E_{\mathrm{KS}}}{\partial\eta}+\frac{\partial E_{\mathrm{TDA}}}{\partial\eta}+\sum_{pqi\sigma}\mathbf{Z}_{pi\sigma}\frac{\partial\mathbf{F}_{pq\sigma}}{\partial\eta}c^{\{0\}}_{qi\sigma}. \tag{41}$$

In Eq. (41) it was assumed that the orthogonality and normalization constraints for the KS and response orbitals is independent from the parameter η. This is true for plane wave basis sets for all of the most important types of perturbations, especially for nuclear displacements.

Using the properties of the target basis set and assuming that η represents a nuclear displacement, Eq. (41) can be further specialized

$$\mathcal{L}^{(\eta)}_{\mathrm{total}}=\sum_{pqi\sigma}(c^{\{0\}}_{pi\sigma})^{\star}\mathbf{F}^{(\eta)}_{pq\sigma}c^{\{0\}}_{qi\sigma}+\sum_{pi\sigma}\sum_{qj\tau}(x_{pi\sigma})^{\star}\mathcal{A}^{(\eta)}_{pi\sigma,qj\tau}x_{qj\tau}+\sum_{pqi\sigma}\mathbf{Z}_{pi\sigma}\mathbf{F}^{(\eta)}_{pq\sigma}c^{\{0\}}_{qi\sigma}, \tag{42}$$

where $\mathcal{B}^{(\eta)}=0$ has been used. This holds again due to the special properties of plane waves. However, if an exchange–correlation functional with nonlinear core corrections is used, there will be a contribution from $\mathcal{B}^{(\eta)}$ that is easily added to Eq. (42). The derivative of the TDA energy can be further simplified,

$$\begin{aligned}\frac{\partial E_{\mathrm{TDA}}}{\partial\eta}&=\sum_{pi\sigma}\sum_{qj\tau}(x_{pi\sigma})^{\star}\mathcal{A}^{(\eta)}_{pi\sigma,qj\tau}x_{qj\tau}\\&=\sum_{pqi\sigma}(x_{pi\sigma})^{\star}\mathbf{F}^{(\eta)}_{pq\sigma}x_{qi\sigma}\\&\quad-\sum_{pji\sigma}\sum_{uv}(x_{pi\sigma})^{\star}(c^{\{0\}}_{ui\sigma})^{\star}\mathbf{F}^{(\eta)}_{uv\sigma}c^{\{0\}}_{vj\sigma}x_{pj\sigma}.\end{aligned} \tag{43}$$

Introducing the density matrices $\mathbf{P}^{(x)}$ and $\mathbf{P}^{(z)}$,

$$\mathbf{P}^{(x)}_{qp\sigma}=\sum_{i}x_{qi\sigma}(x_{pi\sigma})^{\star}+\sum_{rij}x_{rj\sigma}c^{\{0\}}_{pj\sigma}(c^{\{0\}}_{qi\sigma})^{\star}(x_{ri\sigma})^{\star}, \tag{44}$$

$$\mathbf{P}^{(z)}_{qp\sigma}=\sum_{i}\mathbf{Z}_{pi\sigma}c^{\{0\}}_{qi\sigma}, \tag{45}$$

and the corresponding densities $n^{(x)}_{\sigma}$ and $n^{(z)}_{\sigma}$ the total force can be written in compact form as

$$\mathcal{L}^{(\eta)}_{\mathrm{total}}=\sum_{pq\sigma}\mathbf{F}^{(\eta)}_{pq\sigma}(\mathbf{P}_{qp\sigma}+\mathbf{P}^{(x)}_{qp\sigma}+\mathbf{P}^{(z)}_{qp\sigma}). \tag{46}$$

What still needs to be done is the calculation of the Lagrange multipliers Z. They can be determined from the stationarity condition of the total Lagrange function [Eq. (39)] with respect to variations of the KS orbitals,

$$\frac{\partial\mathcal{L}_{\mathrm{total}}}{\partial c^{\{0\}}}=0. \tag{47}$$

Making again use of the fact that the derivatives are taken at the point of optimized KS orbitals one arrives at a system of linear equations for Z,

$$\sum_{qj}(\mathbf{F}_{pq\sigma}\delta_{ij}-\epsilon_{ij\sigma}\delta_{pq})\mathbf{Z}^{\star}_{qj\sigma}+\sum_{qr}\mathbf{Q}_{pr\sigma}\mathbf{W}_{rq\sigma}[n^{(z)}]c^{\{0\}}_{qi\sigma}=u_{pi\sigma}. \tag{48}$$

Equation (48) has the same form as the coupled perturbed KS equations from static density functional perturbation theory. It only differs from these equations by its right-hand side u to be derived below. From Eq. (48) it also becomes clear that Z fulfills the same orthogonality constraint as a linear response orbital,

$$\sum_{p}\mathbf{Z}_{pi\sigma}c^{\{0\}}_{pj\sigma}=0, \tag{49}$$

and therefore has the correct number of degrees of freedom. Equation (48) is known as the Handy–Schaefer Z vector equation.[36] The vector u is calculated from

$$u_{pi\sigma}=\sum_{rk\kappa}\sum_{qj\tau}(x_{rk\kappa})^{\star}\frac{\partial(\mathcal{A}+\mathcal{B})_{rk\kappa,qj\tau}}{\partial(c^{\{0\}}_{pi\sigma})^{\star}}x_{qj\tau}. \tag{50}$$

Special care has to be taken to include the projections on the virtual states correctly. The final result is

$$\begin{aligned}u_{pi\sigma}=\sum_{rq}\mathbf{Q}_{pr\sigma}\Big\{&\mathbf{W}_{rq\sigma}[n^{(x)}]c^{\{0\}}_{qi\sigma}+\mathbf{W}_{rq\sigma}[n^{\{1\}}]x_{qi\sigma}\\&+x_{rj\sigma}\sum_{s}((c^{\{0\}}_{qj\sigma})^{\star}\mathbf{W}_{qs\sigma}[n^{\{1\}}]c^{\{0\}}_{si\sigma})\\&+\mathbf{W}^{(2)}_{rq\sigma}[n^{\{1\}}]c^{\{0\}}_{qi\sigma}\Big\},\end{aligned} \tag{51}$$

where $\mathbf{W}^{(2)}$ is the matrix representation of the potential from the third functional derivative of the exchange–correlation energy,

$$\mathbf{W}^{(2)}_{pq\sigma}(\delta n)=\int d\mathbf{r}\,\varphi^{\star}_{p}(\mathbf{r})\varphi_{q}(\mathbf{r})\sum_{\tau,\kappa}\int d\mathbf{r}'\,d\mathbf{r}''\times\frac{\delta^{3}E_{\mathrm{xc}}}{\delta n_{\sigma}(\mathbf{r})\,\delta n_{\tau}(\mathbf{r}')\,\delta n_{\kappa}(\mathbf{r}'')}\bigg|_{n^{\{0\}}}n^{\{1\}}_{\tau}(\mathbf{r}')n^{\{1\}}_{\kappa}(\mathbf{r}''). \tag{52}$$

III. EXAMPLE CALCULATIONS

Calculations of excited state geometries and harmonic vibrational spectra of formaldehyde have been performed. This molecule was chosen as it has been extensively used as a benchmark in excited state calculations at various levels of theory.

The methods described in the preceding section have been implemented into the Car–Parrinello molecular dynam-

TABLE I. Calculated equilibrium structures and adiabatic excitation energies (eV) compared to experiment and calculations from literature. All density functional based values calculated with the PBE (Ref. 41) functional. Bond lengths are given in Å, angles in degrees. Φ denotes the out-of-plane angle.

Method	R_{CO}	R_{CH}	$\angle_{HCH}$	Φ	ΔE	Reference
			State $^1A_1$			
DFT	1.211	1.118	116.1	0		This work
CCSD(T)	1.2075	1.1008	116.3	0		43
MR–AQCC	1.206	1.099	116.7	0		45
Expt.	1.2033	1.1005	116.2	0		47
			State $^1A''(n-\pi^*)$			
TDA	1.308	1.103	116.8	30.0	3.53	This work
TDDFT	1.31	1.10	116	33	3.42	18
TDDFT	1.308	1.106	116.2	34.3	3.50[a]	17
MRDCI	1.334	1.116	120.2	34.5	3.50	44
Expt.	1.323	1.098	118.4	34.0	3.49	47
			State $^1B_2(n-3s)$			
TDA	1.204	1.115	119.0	0	5.70	This work
MR–CISD	1.216	1.131	125.2	0	7.09	46
MRD–CI	1.243	1.140	123.9	0	7.00	44
			State $^3A''$			
TDA	1.305	1.108	113.7	43.2	2.67	This work
TDDFT	1.31	1.11	111	48	2.53[a]	18
Expt.	1.307	1.084	121.8	41.1	3.12	47

[a]Values include ZPE differences.

ics code CPMD[37] version 3.6. The calculations have been performed at a plane wave cutoff of 90 Rydberg within a cubic computational box of 25 Bohr length. The method of Martyna and Tuckerman[38] was used to decouple periodic images in the electrostatic potential. Pseudopotentials of the Troullier–Martins[39] type within the Kleinman–Bylander[40] scheme have been employed to eliminate core electrons and the cusp at the hydrogen nuclei. Cutoff radii for the pseudopotentials were 0.5, 1.05, and 1.23 Bohr for hydrogen, oxygen, and carbon, respectively. Nonlocal pseudopotentials were used for s angular momentum for carbon and oxygen only. All calculations were done using the PBE[41] gradient corrected exchange and correlation functional. Harmonic vibrational frequencies were calculated by two point finite differences using a step length of 10^{-2} a.u.

In Table I optimized geometries and adiabatic excitation energies for the $^1A''$, $^1B_2$, and the first triplet state $^3A''$ are presented. Results for the ground state geometry are included for comparison. Table II shows harmonic vibrational frequencies for the same states. All results are compared to other calculations based on linear response to time-dependent density functional theory or high-level wave-function based methods and experiments. The calculated TDA adiabatic excitation energies are close to the results from TDDFT and MRCI. Due to the fact that no asymptotic correction[42] to the exchange and correlation potential was applied to the excitation energy of the Rydberg state $^1B_2$ is largely underestimated (1.3 eV). However, the optimized geometry in this state does not show this pathology. Deviations from the MR–CI values are slightly larger than for the other states but still within acceptable range. That the asymptotic behavior of the functional only affects the excitation energy,

TABLE II. Calculated harmonic vibrational frequencies (cm^{-1}) compared to experiment and calculations from literature. All density functional based values calculated with the PBE (Ref. 41) functional. Experimental frequencies for the ground state are corrected for anharmonicity.

Method	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	Reference
				State $^1A_1$			
DFT	1146	1236	1472	1749	2781	2840	This work
MR–CISD	1176	1250	1534	1720	3005	3088	46
Expt.	1191	1288	1563	1764	2944	3009	48
				State $^1A''(n-\pi^*)$			
TDA	524	1111	1230	1280	2910	3065	This work
TDDFT		855	1254	1294	2916	3016	18
TDDFT	619	853	1246	1288	2905	3008	17
Expt.		904	1183	1293	2846	2968	47
				State $^1B_2(n-3s)$			
TDA	870	1084	1183	1612	2709	2984	This work
MR–CISD	868	1070	1097	1602	2562	2858	46
Expt.	822			1577	2275		47
				State $^3A''$			
TDA	713	970	1210	1289	2843	2975	This work
TDDFT				1261			18
Expt.				1283			47

not the optimized geometries was already found in Ref. 49. The only noticeable differences in the optimized TDA and TDDFT structures are for the out-of-plane dihedral angles of the $^1A''$ and $^3A''$ states and for the HCH angle in the triplet state. For the triplet state the TDA values are slightly closer to the experimental values. It is noticed that the symmetric and antisymmetric stretch vibration for the ground state are underestimated by about $200\,\mathrm{cm}^{-1}$. It was verified by an independent calculation that this is a feature of the PBE functional and not due to the pseudopotentials or plane wave basis set. However, for the Rydberg $^1B_2$ state the same vibrations are too large by about $100\,\mathrm{cm}^{-1}$. If this is due to the TDA it cannot be concluded from the present calculation. There is one other vibration where the TDA calculation results in a substantially higher frequency than the corresponding TDDFT calculations. The CH_2 rocking mode (ν_2) of the $n-\pi^*$ state is overestimated by $250\,\mathrm{cm}^{-1}$. However, the experimental value for this vibration, including anharmonicity effects, is lying in between the calculated TDDFT and TDA values.

Compared to other theoretical methods and experimental values an overall good agreement for the structural features of three excited states of formaldehyde was achieved with the TDA within the pseudopotential/ plane wave framework.

IV. DISCUSSION AND SUMMARY

A computationally efficient method for the calculation of excitation energies from time-dependent density functional theory has been presented. The method is specially adapted to the needs of calculations within the pseudopotential/plane wave basis set framework. In contrast to earlier methods the transformation of the Kohn–Sham matrix into a diagonal representation is avoided. Instead projection operators on the virtual space are used. This technique has been in use in density functional perturbation theory[24,25] using plane wave basis sets for some time now. Similar methods have been proposed for linear scaling algorithms.[34,50]

Using a Lagrangian technique derivatives to the excitation energies in the Tamm–Dancoff approximation have been calculated. This method has been applied to calculate the nuclear gradients of the excited state hypersurface. As a first application the adiabatic excitation energies, optimized geometries and harmonic vibrations of three states of formaldehyde have been calculated. Good agreement to other TDDFT calculations and multireference CI calculations as well as experiments was achieved. As was found for vertical excitation energies, the Tamm–Dancoff approximation has the potential to be a useful alternative to the TDDFT for exploring excited state surfaces and the calculation of excited state properties. However, calculations on more systems and a wider set of excited states have to be performed to verify this.

The methods presented in this paper will serve as a starting point for many different applications. The use of a plane wave basis set allows for an easy extension to the condensed phase. The application of TDDFT within solid state theory is by no means trivial[23] and a lot of work needs to be done. However, for special applications like localized excitations of molecules in solution the current theoretical status should be sufficient and allow for interesting applications. In addition, the use of TDDFT methods in QM/MM frameworks[51,52] is straightforward, at least for the calculation of vertical excitation energies.

APPENDIX A: FORCES IN THE PLANE WAVE/ PSEUDOPOTENTIAL FRAMEWORK

Plane waves are defined with respect to a periodic computational box with volume Ω,

$$\varphi_p(\mathbf{r}) = \frac{1}{\Omega}\exp[iG_p\cdot\mathbf{r}], \tag{A1}$$

where G_p denotes a reciprocal lattice vector. A basis set comprises all plane waves with a kinetic energy smaller than a given energy cutoff

$$\tfrac{1}{2}G^2 \leqslant E_{\mathrm{cutoff}}. \tag{A2}$$

In order to keep the basis set at a manageable size, pseudopotentials have to be used to remove highly localized core orbitals. For computational reasons the pseudopotentials are used in a fully separable form. Within this framework the Kohn–Sham matrix reads

$$\mathbf{F}_{pq\sigma} = \frac{1}{2}G_p^2\delta_{pq} + V^{\sigma}_{\mathrm{loc}}(G_p - G_q) + \sum_I \sum_{s,t} P^{\star}_{I,s}(G_p)S^{\star}_I(G_p)h^I_{st}P_{I,t}(G_q)S_I(G_q), \tag{A3}$$

where the local potential is

$$V^{\sigma}_{\mathrm{loc}}(G) = \sum_I V^{\mathrm{pp}}_{\mathrm{loc}}(G)S_I(G) + V_{\mathrm{xc}}(G) + 4\pi\frac{n_{\mathrm{tot}}(G)}{G^2}, \tag{A4}$$

with $V^{\mathrm{pp}}_{\mathrm{loc}}$ the local pseudopotential functions, $S_I(G) = \exp[-iG\cdot R_I]$ the structure factor, and n_{tot} the sum of the electron density and the nuclear compensation charges,

$$n_{\mathrm{tot}}(G) = n(G) + \sum_I n^{\mathrm{core}}_I(G)S_I(G). \tag{A5}$$

The Kohn–Sham matrix depends on the nuclear positions only through the structure factors S_I. The derivative of S_I with respect to R_I is easily calculated in reciprocal space

$$\frac{\partial S_I(G)}{\partial R_{I,u}} = -iG_uS_I(G). \tag{A6}$$

Therefore the derivatives of the Kohn–Sham matrix can be written as (using $G = G_p - G_q$)

$$\frac{\partial F_{pq\sigma}}{\partial R_{I,u}} = -iG_uV^{\mathrm{pp}}_{\mathrm{loc}}(G)S_I(G) - 4\pi iG_u\frac{n^{\mathrm{core}}_I(G)}{G^2}S_I(G) + iG_p\sum_{s,t} P^{\star}_{I,s}(G_p)S^{\star}_I(G_p)h^I_{st}P_{I,t}(G_q)S_I(G_q) - iG_q\sum_{s,t} P^{\star}_{I,s}(G_p)S^{\star}_I(G_p)h^I_{st}P_{I,t}(G_q)S_I(G_q). \tag{A7}$$

All densities (n, $n^{\{1\}}$, $n^{(x)}$, $n^{(z)}$) can be calculated efficiently using standard Fourier transform techniques. The potentials are calculated either on the corresponding real space grid or in Fourier space.

APPENDIX B: DERIVATIVES OF THE EXCHANGE–CORRELATION FUNCTIONAL

The algorithms presented need higher derivatives of the exchange–correlation energy to be calculated. This leads to complicated but manageable expressions in the case of gradient corrected functionals. In plane wave calculations it is common usage to evaluate the exchange–correlation energy and potentials on the same real space grid as used in Fourier transforms. Even for the standard potential care has to be taken as not to introduce high Fourier components in intermediate quantities. This problem is even worse for the higher derivatives needed in TDKS. However, as mentioned in Ref. 53 the necessary potentials can also be calculated using finite difference techniques. This can be done efficiently as the potentials are only needed along the linear response density.

The potentials needed in the force calculation of the Tamm–Dancoff energy surface are

$$W_\sigma^{(1)}(\mathbf{r}) = \sum_\tau \int d\mathbf{r}' \frac{\delta^2 E_{\mathrm{xc}}}{\delta n_\sigma(\mathbf{r})\,\delta n_\tau(\mathbf{r}')}\bigg|_{n^{\{0\}}} n_\tau^{\{1\}}(\mathbf{r}') \tag{B1}$$

and

$$W_\sigma^{(2)}(\mathbf{r}) = \sum_{\tau,\kappa} \int d\mathbf{r}'\, d\mathbf{r}'' \frac{\delta^3 E_{\mathrm{xc}}}{\delta n_\sigma(\mathbf{r})\,\delta n_\tau(\mathbf{r}')\,\delta n_\kappa(\mathbf{r}'')}\bigg|_{n^{\{0\}}} \times n_\tau^{\{1\}}(\mathbf{r}') n_\kappa^{\{1\}}(\mathbf{r}''). \tag{B2}$$

Finite difference approximations to $W^{(1)}$ and $W^{(2)}$ can be calculated using central difference formulas

$$W_\sigma^{(1)}(\mathbf{r}) \approx \sum_k \frac{a_k}{\epsilon} V_{\mathrm{xc}}^\sigma(n^{\{0\}} + k\epsilon n^{\{1\}}), \tag{B3}$$

$$W_\sigma^{(2)}(\mathbf{r}) \approx \sum_l \frac{b_l}{\epsilon^2} V_{\mathrm{xc}}^\sigma(n^{\{0\}} + l\epsilon n^{\{1\}}). \tag{B4}$$

Numerical tests have shown that stable results can be achieved with $\epsilon = 5\times 10^{-4}$ with a three point formula for $W^{(1)}$ ($a_k = 1,0,1$ for $k = -1,0,1$) and a five point formula for $W^{(2)}$ ($b_l = -1,16,-30,16,-1$ for $l = -2,-1,0,1,2$).

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